



Ionic liquid-catalyzed selective production of hydrofluoroether: Synthesis of a third generation CFC alternative, $\text{CF}_3\text{CH}_2\text{OCHFCF}_2\text{CF}_3$

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ARTICLE INFO

Article history:

Received 7 August 2008

Received in revised form 20 November 2008

Accepted 5 December 2008

Available online 11 December 2008

Keywords:

Hydroalkoxylation

Hexafluoropropene

2,2,2-Trifluoroethanol

Ionic liquid

CFC alternatives

ABSTRACT

A hydrofluoroether, one of the third generation chlorofluorocarbon (CFC) alternatives, $\text{CF}_3\text{CH}_2\text{OCHFCF}_2\text{CF}_3$ was obtained in high yield and selectivity from the hydroalkoxylation reaction of hexafluoropropylene and 2,2,2-trifluoroethanol conducted in the presence of an imidazolium-based ionic liquid catalyst such as 1-butyl-3-methylimidazolium acetate, 1-butyl-3-methylimidazolium bicarbonate, or 1-butyl-3-methylimidazolium carbonate. By using these ionic liquids, the formation of difficult-to-remove unsaturated side products was effectively suppressed.

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1. Introduction

Hydrofluoroethers (HFEs) have been considered as the most promising candidates for refrigerants, cleaning solvents, and blowing agents to replace chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs), due to their zero ozone depleting potential, low global warming potential, and favorable physical and chemical properties including low surface tension, non-flammability, and excellent solvating ability [1–4]. HFEs have also been regarded as an important class of fluorinated organic compounds for many potential applications: heat transfer media, particulate removal and carrier fluids, buffering abrasive agents, displacement drying agents, power cycle working fluids, and clinical usages [5–9].

Numerous methods have been reported to produce HFEs including the fluorination of ether with F_2 [10,11] or metal fluoride [12], the electrochemical fluorination of ether [13], and the alkylation of acyl halides using a sulfonic acid ester as an alkylating agent in the presence of anhydrous KF [14,15]. However, these methods suffer from either the low product selectivity or the difficulty in handling the hazardous and reactive raw materials. HFEs can also be obtained from the hydroalkoxylation reaction of

commercially available fluorinated olefins (tetrafluoroethylene and hexafluoropropylene) in the presence of a base catalyst or free radical initiator [16–22], but these methods either require long reaction time or produce relatively large amounts of unsaturated HFEs were always co-produced, which are difficult to remove by distillation due to the closeness in boiling points between saturated and unsaturated HFEs.

Recently, Matsukawa et al. reported that the formation of commonly observed unsaturated olefinic side products could be completely suppressed by using a Pd^0 complex, $[\text{Pd}(\text{PPh}_3)_4]$ as the catalyst for the hydroalkoxylation of fluoroolefins [23]. This is a great finding, but the use of an expensive Pd complex seems to be a major obstacle in the commercial application of this process.

Ionic liquids such as 1-ethyl-3-methylimidazolium tetrafluoroborate ($[\text{EMIm}] \text{BF}_4^-$) and 1-ethyl-3-methylimidazolium hexafluorophosphate ($[\text{EMIm}] \text{PF}_6^-$) were also employed as catalysts and reaction media for the hydroalkoxylation of fluoroolefins, but the yields of HFEs were not high even at elevated temperatures and long reaction time [24], possibly due to the lack of basicity of $[\text{EMIm}] \text{BF}_4^-$ and $[\text{EMIm}] \text{PF}_6^-$.

Since base catalysts such as NaOH and KF [16–21] are known to be highly active for the hydroalkoxylation of fluoroolefins, it is easily conceivable that a basic ionic liquid could proceed the hydroalkoxylation more effectively than the neutral ionic liquids, $[\text{EMIm}] \text{BF}_4^-$ and $[\text{EMIm}] \text{PF}_6^-$. It is also expected that the unique properties of ionic liquids could suppress the formation of olefinic side products. In this context, we have tested the performance of

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basic ionic liquids for the hydroalkoxylation of fluoroolefins to produce HFEs.

Herein, we report that imidazolium-based ionic liquids with a strongly basic anion such as CH_3CO_2^- (AcO^-), CO_3^{2-} , and HCO_3^- are highly effective for the hydroalkoxylation of hexafluoropropene (HFP, **1**) with 2,2,2-trifluoroethanol (TFE, **2**), producing a saturated HFE ($\text{CF}_3\text{CH}_2\text{OCF}_2\text{CHFCF}_3$, **3**) in high yield and selectivity.

2. Experimental

2.1. Materials

TFE, KF, K_2CO_3 , potassium acetate (AcOK), imidazole, 1-methylimidazole, dimethylacetamide (DMAc), $[\text{BMIm}]\text{BF}_4^-$, $[\text{BMIm}]\text{PF}_6^-$, and $[\text{BMIm}]\text{Cl}$ were purchased from Aldrich Chemical Co. and used as received. TFE was obtained from TCI Co. and used without further purification. $\text{CF}_3\text{CH}_2\text{OCF}_2\text{CHFCF}_3$ and HFP were obtained from Ulsan Chemical Co. and SynQuest Lab. Inc., respectively. $[\text{BMIm}]\text{HCO}_3^-$, $[\text{BMIm}]\text{CO}_3^{2-}$, $[\text{BMIm}]\text{AcO}^-$, methylimidazolium acetate $[\text{HMIm}]\text{AcO}^-$, imidazolium acetate $[\text{HIm}][\text{AcO}^-]$, 1-butyl-2,3-dimethylimidazolium acetate ($[\text{BDMIm}]\text{AcO}^-$), 1-ethyl-3-methylimidazolium acetate ($[\text{EMIm}]\text{AcO}^-$), and 1-hexyl-3-methylimidazolium acetate ($[\text{HexMIm}]\text{AcO}^-$) were prepared according to the literature procedures [25–27].

2.2. Hydroalkoxylation of HFP

All the reactions were conducted in a 100-mL stainless-steel bomb reactor equipped with a magnet bar, a thermocouple, a sampling port, and a pressure gauge. The reactor was charged with an appropriate catalyst, TFE, DMAc, and dibutylether as an internal standard and was pressurized with 0.4 MPa of HFP. The bomb reactor was then stirred at a room temperature. After the completion of the reaction, the reactor was cooled to -10°C and the product mixture was analyzed by a Hewlett Packard 6890 gas chromatograph equipped with a flame ionized detector (FID), and a HP-FFAP capillary column ($30\text{ m} \times 0.32\text{ mm} \times 0.25\text{ }\mu\text{m}$) or a PoraPLOT Q capillary column ($30\text{ m} \times 0.32\text{ mm} \times 0.25\text{ }\mu\text{m}$). ^1H NMR spectra were recorded on a Varian UNITYplus-300.

0.2 μL of the pre-cooled product mixture contained in a 10- μL Hamilton syringe was injected into the GC through a septum placed on the top of the injector. The yield ($100 \times$ moles of desired product/initial moles of TFE) of the major product ($\text{CF}_3\text{CH}_2\text{OCF}_2\text{CHFCF}_3$, **3**) and the conversion of TFE ($100 \times$ moles of TFE converted/initial moles of TFE) were determined from a calibration curve made using authentic samples (**3** and TFE) and the internal standard (dibutylether). The combined yield of low boiling side products, **4–6** ($\text{cis}/\text{trans}-\text{CF}_3\text{CF}=\text{CFOCH}_2\text{CF}_3$ and $\text{CF}_2=\text{CFCF}_2\text{OCH}_2\text{CF}_3$) was calculated based on the GC area ratio (yield of **3** \times area of a side product/area of **3**) and the ^1H NMR integration ratio of side product/**3** because authentic samples for side products were not commercially available. For the analysis by GC, it was assumed that compounds **3–6** have the same FID response factor.

The combined yield of doubly alkoxylated side products, **7–8** ($\text{CF}_3\text{CHFCF}(\text{OCH}_2\text{CF}_3)_2$ and $\text{CF}_3\text{CH}_2\text{OCF}_2\text{CHFOCH}_2\text{CF}_3$) was obtained from a calibration curve made using dibutylether and a crude mixture of **7–8** (purity: approximately 92%) recovered from a distillation. Each GC sample was injected three times and the results were averaged to reduce the experimental errors. The uncertainty of the measurements was estimated as 2–3%.

2.3. Product characterization

Characterization of products was conducted using a Hewlett Packard 6890-5973 MSD GC-Mass spectrometer equipped with a

PoraPLOT Q capillary column. Mass spectra of 3–8 representative fragmentation peaks for each product component are provided below (see also Fig. S-1 in the Supplementary Material).

$\text{CF}_3\text{CHFCF}_3$: m/z 151 (M–HF), 101 (M– CF_3), 69 (CF_3); $\text{CHFCF}_2\text{OCH}_2\text{CF}_3$, **3**: m/z 231 (M–HF), 131 (M– CF_3), 151 ($\text{CF}_3\text{CHFCF}_2$), 83 (CF_3CH_2), 69 (CF_3); $\text{cis}/\text{trans}-\text{CF}_3\text{CF}=\text{CFOCH}_2\text{CF}_3$, **4**, **5**: m/z 230 (M $^+$), 211 (M–F), 83 (M– $\text{CF}_3\text{CH}_2\text{O}$), 69 (CF_3); $\text{CF}_2=\text{CFCF}_2\text{OCH}_2\text{CF}_3$, **6**: m/z 230 (M $^+$), 180 (M– CF_2), 149 (M– $\text{CF}_2=\text{CF}$), 131 (M– $\text{CF}_3\text{CH}_2\text{O}$), 83 (CF_3CH_2), 69 (CF_3); $\text{CF}_3\text{CHFCF}(\text{OCH}_2\text{CF}_3)_2$, **7**: m/z 311 (M–HF), 231 (M– $\text{CF}_3\text{CH}_2\text{O}$), 83 (CF_3CH_2); $\text{CF}_3\text{CH}_2\text{OCF}_2\text{CHFOCH}_2\text{CF}_3$, **8**: m/z 311 (M–HF), 181 ($\text{CHFCF}_2\text{OCH}_2\text{CF}_3$), 149 ($\text{CF}_3\text{CH}_2\text{OCF}_2$), 83 ($\text{CF}_3\text{CH}_2\text{O}$).

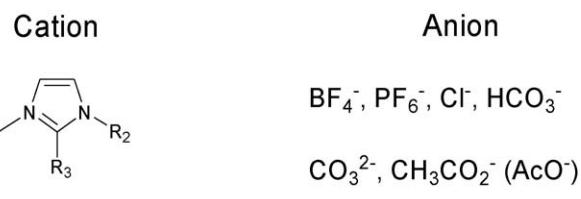
3. Results and discussion

3.1. Activities of imidazolium-based catalysts

The hydroalkoxylation reaction of HFP with TFE was investigated in DMAc for 1 h at an ambient temperature and at the molar ratio of TFE/catalyst = 50 in the presence of an imidazolium-based ionic liquid shown in Scheme 1.

For comparison, the activities of potassium salts were also tested under the same experimental condition. As listed in Table 1, KF, AcOK, and K_2CO_3 were highly active for the hydroalkoxylation, resulting in almost quantitative conversion of TFE. However, these potassium salt catalysts were not very selective for the production of **3**, due to the co-production of unsaturated HFEs ($\text{cis}-\text{CF}_3\text{CF}=\text{CFOCH}_2\text{CF}_3$, **4**, $\text{trans}-\text{CF}_3\text{CF}=\text{CFOCH}_2\text{CF}_3$, **5**, and $\text{CF}_2=\text{CFCF}_2\text{OCH}_2\text{CF}_3$, **6**) in yield of about 10% as well as small amounts of over hydroalkoxylated HFEs (see Scheme 2).

As already mentioned, the formation of such olefinic HFEs is a headache in the purification of **3** by distillation because compounds **4–6** have close boiling points to that of **3**. It is reported that, in the hydroalkoxylation of HFP with TFE using a potassium salt catalyst, the formation of unsaturated HFEs are inevitable because K^+ is capable of eliminating β -fluoride from the carbanion intermediate ($\text{CF}_3\text{C}^-\text{FCF}_2\text{OCH}_2\text{CF}_3$), formed by the addition of $\text{CF}_3\text{CH}_2\text{O}^-$ to **1** [23]. It is also proposed that the activity of alkali metal fluoride (MF) and the product composition is greatly affected by the degree of dissociation of MF into M $^+$ and F $^-$ in a polar aprotic solvent and by the size of M $^+$ [28]. These observations strongly suggest that the formation of unsaturated HFEs **4–6** can be controlled to a certain extent by designing a catalyst with a suitable combination of cation and anion. In this context, imidazolium-based ionic liquids were chosen as alternative catalysts because their physical and chemical properties can be easily tailored by varying anions and/or cations [26]. It is hoped that the acidic C-2 hydrogen of the imidazolium ring could contribute to the stabilization of a plausible active species, $\text{CF}_3\text{CH}_2\text{O}^-$, through a hydrogen bonding. However, contrary to our expectation, $[\text{BMIm}]\text{BF}_4^-$ and $[\text{BMIm}]\text{PF}_6^-$ exhibited almost no



[BMIm]: $\text{R}_1=\text{butyl}$, $\text{R}_2=\text{methyl}$, $\text{R}_3=\text{H}$
[HIm]: R_1 , R_2 , $\text{R}_3=\text{H}$
[BDMIm]: $\text{R}_1=\text{butyl}$, R_2 , $\text{R}_3=\text{methyl}$
[EMIM]: $\text{R}_1=\text{ethyl}$, $\text{R}_2=\text{methyl}$, $\text{R}_3=\text{H}$
[HexMIm]: $\text{R}_1=\text{hexyl}$, $\text{R}_2=\text{methyl}$, $\text{R}_3=\text{H}$

Scheme 1. Structures of ionic liquids used for the hydroalkoxylation of HFP.

Table 1

Activities of various potassium and imidazolium-based catalysts for the hydroalkoxylation of HFP^a.

Entry	Catalyst	TFE conv. (%)	Yield (%)		
			3	4–6	7–8
1	KF	100	89.6	10.3	0.1
2	K ₂ CO ₃	99.2	89.4	9.6	0.2
3	AcOK	100	90.5	9.2	0.3
5	[BMIm]BF ₄	0.6	0.5	0.1	–
6	[BMIm]PF ₆	0.7	0.6	0.1	–
7	[BMIm]Cl	26.5	23.4	2.8	0.3
8	[BMIm]AcO	98.2	96.5	0.8	0.9
9	[BMIm]HCO ₃	95.1	93.3	0.8	1.0
10	[BMIm] ₂ CO ₃	96.8	94.6	1.0	1.2
11	Bu ₄ NOAc	15.3	14.1	1.0	0.2
12 ^b	[BMIm]AcO	31.4	29.5	1.8	0.1–0.2
13 ^b	[BMIm] ₂ CO ₃	59.6	56.3	2.1	0.2–0.3
14 ^b	[BMIm]HCO ₃	42.9	40.6	2.2	0.1

^a Molar ratio of TFE/catalyst = 50 (TFE = 100 mmol), solvent = DMAc (10 mL), temperature = 25 °C, reaction time = 1 h.

^b Molar ratio of TFE/catalyst = 150 (TFE = 100 mmol).

activity, and [BMIm]Cl showed only moderate activity under the experimental condition (Table 1). It seems that the basicities of the anions of these ionic liquids are not strong enough to generate CF₃CH₂O[–] through the interaction with the weakly acidic hydroxyl group of TFE.

In contrast to [BMIm]BF₄, [BMIm]PF₆, and [BMIm]Cl, imidazolium-based ionic liquids with a strongly basic anion, CH₃CO₂[–] (AcO[–]), was highly active for the hydroalkoxylation. The yield of 3 reached to 96.5% at the molar ratio of TFE/[BMIm]AcO = 50 when [BMIm]AcO was used as the catalyst. More importantly, the formation of unsaturated side products, 4–6 was greatly reduced down to 0.8%. This is a significant improvement when compared with the hydroalkoxylation in the presence of a potassium salt.

[BMIm]HCO₃ and [BMIm]₂CO₃ showed similar activity to [BMIm]AcO, producing 3 in high yields and selectivities, whereas [BMIm]Cl exhibited much lower activity. These results may imply that the imidazolium salt with an anion of a weak acid is more effective for the activation of TFE than those with an anion of a strong acid in the hydroalkoxylation of HFP with TFE. Considering the pK_a values of HCl (–7.00), AcOH (4.75), H₂CO₃ (6.35), and HCO₃[–] (10.33), the lower activity of [BMIm]Cl can be ascribed to the weaker basicity of Cl[–] (conjugate base of HCl) compared with those of AcO[–], HCO₃[–] and CO₃^{2–} because more basic anion should provide more stronger interaction with the hydroxyl group of TFE, thereby facilitating the activation of TFE to generate an active species, CF₃CH₂O[–] [29,30].

The effect of anion is more pronounced at higher molar ratio of TFE/catalyst at 150 (see Table 2, entry 12–14). The imidazolium salt with the most basic CO₃^{2–} showed the highest activity,

Table 2

Effect of the degree of alkyl substitution on the activity of imidazolium acetate^a.

Entry	Catalyst	TFE conv. (%)	Yield (%)		
			3	4–6	7–8
1	[HIm]AcO	6.6	0.1	6.5	–
2	[MIM]AcO	73.2	62.9	9.0	1.3
3	[BMIm]AcO	98.2	96.5	0.8	0.9
4	[BDMIm]AcO	100	98.8	0.4	0.8
5	[EMIm]AcO	97.8	96.3	0.9	0.6
6	[HexMIm]AcO	98.6	97.0	0.7	0.9

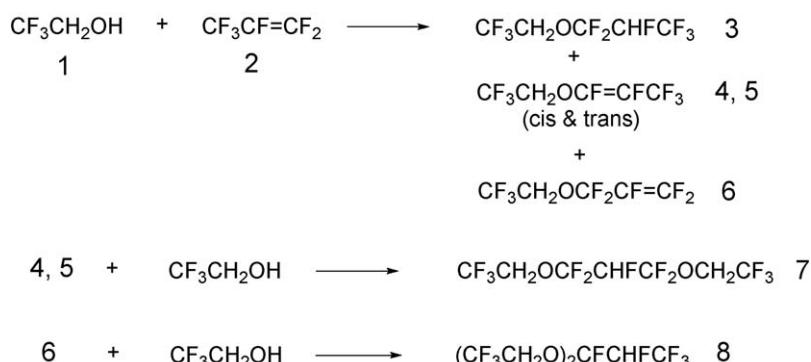
^a Molar ratio of TFE/catalyst = 50 (TFE = 100 mmol), solvent = DMAc (10 mL), temperature = 25 °C, reaction time = 1 h.

whereas the least basic AcO gave the lowest activity. However, at the higher molar ratio of TFE/catalyst, the increased formation of side products was also observed. It is noteworthy that the activity of tetrabutylammonium acetate (Bu₄NOAc) is much lower than that of [BMIm]AcO, demonstrating the important role of imidazolium ring. It is likely that the basicity of AcO[–] and the consequent interaction with TFE seems to be enhanced by the presence of a bulky imidazolium ring.

3.2. Effect of alkyl substituents on the imidazolium ring

The effect of alkyl substitution on the imidazolium ring was also investigated in the presence of an imidazolium acetate at the molar ratio of TFE/catalyst = 50. The degree of alkyl substitution on the imidazolium ring exerted a pronounced effect on the catalytic activity. As listed in Table 2, the imidazolium acetate with two or three alkyl groups on the imidazolium ring showed much higher activity than those containing none or one alkyl group on the imidazolium ring. The activity of the imidazolium acetate was found in the order of increasing electron density on the imidazolium ring: [BDMIm]AcO > [BMIm]AcO > [MIM]AcO > [HIm]AcO. The increase of the electron donation from the alkyl group or groups to the imidazolium ring will contribute to the increase of the electron density on the imidazolium ring, consequently resulting in the weakening of the electrostatic interaction between imidazolium cation and acetate anion. As a result, the hydrogen abstraction from TFE becomes more feasible for the generation of an active species, CF₃CH₂O[–].

It is also noteworthy that the formation of unsaturated HFEs decreased with the increasing electron density on the imidazolium ring, i.e., with the decreasing acidity of the imidazolium cation. The reduction in the acidity on the imidazolium cation is likely to limit the interaction with the carbanion intermediate, and thus the formation of unsaturated HFEs through the F[–] abstraction from the carbanion intermediate seems to be suppressed. These results strongly imply that the formation of unsaturated side



Scheme 2. Structures of the products from the hydroalkoxylation of HFP with TFE.

Table 3Effect of molar ratio of TFE/[BMIm]AcO on the hydroalkoxylation of HFP^a.

Entry	Molar ratio (TFE/[BMIm]AcO)	TFE conv. (%)	Yield (%)		
			3	4–6	7–8
1	100	91.9	88.6	2.2	1.1
2	50	98.2	96.5	0.8	0.9
3	30	100	98.4	0.4	0.8
4	20	100	99.0	0.3	0.7
5	15	100	99.4	0.2	0.4

^a TFE = 100 mmol, solvent = DMAc (10 mL), temperature = 25 °C, reaction time = 1 h.

products, **4–6** could be further reduced if a methyl group or groups are replaced by a functional group or groups with better electron-donating ability. The effect of alkyl chain length on the activity was also evaluated, but any noticeable change in activity was not observed with the variation of the alkyl chain.

3.3. Effect of catalyst concentration

Table 3 shows the change of TFE conversion and product composition with the molar ratio of TFE/[BMIm]AcO for the hydroxyalkoxylation reactions of HFP conducted in DMAc for 1 h. The conversion of TFE and the yield of **3** increased gradually with the decreasing molar ratio of TFE/[BMIm]AcO, while decreasing the formation of side products, **4–6**. The simultaneous increase of the yield and selectivity of the major product is an important advantage of the imidazolium acetate catalyst in terms of industrial point of view. One may suspect that the olefinic side products could be produced by the elimination of HF from **3**. However, such a pathway to the formation of olefinic side products was excluded because any transformation of **3** was not observed when **3** was reacted with TFE or HFP in the presence of [BMIm]AcO in DMAc. From these results, it is concluded that the side product is not the outcome of the secondary reaction of **3** and thus the formation of side products can be further reduced by performing the hydroalkoxylation reaction at higher concentration of a suitable catalyst.

3.4. Effect of reaction time

Effect of reaction time was also examined using [BMIm]AcO at 25 °C. The molar ratio of TFE/[BMIm]AcO was set at 50. A small amount (0.3 mL) of sample was periodically taken out of the reactor through the sampling port and analyzed by GC. As shown in **Fig. 1**, the conversion of HFP increased continuously with the reaction time and reached the maximum of 100% at 40 min. Any change in conversion was not observed thereafter up to 120 min. In contrast, yield of **3** decreased slightly after 40 min due to the increase of the side products.

3.5. Plausible reaction mechanism

Based on the experimental results, plausible pathways to the formation of **3** and side products in the presence of [BMIm]AcO are depicted in **Scheme 3**. TFE is likely to be activated first by AcO[–] of [BMIm]AcO to generate CF₃CH₂O[–], and AcOH. CF₃CH₂O[–] would then interact with HFP to form a transient carbanionic intermediate **A** (CF₃C[–]FCF₂OCH₂CF₃), which in turn transforms into **3** upon interaction with TFE or AcOH along with the generation of CF₃CH₂O[–] or AcO[–]. Alternatively, F[–] can also be abstracted by [BMIm]⁺ from the intermediate species **A** to give olefinic side products **4–6** and [BMIm]F, but the process would be much slower because the resulting [BMIm]F is highly unstable. Further alkoxylation of **4–6** with TFE would produce **7** and **8**. The

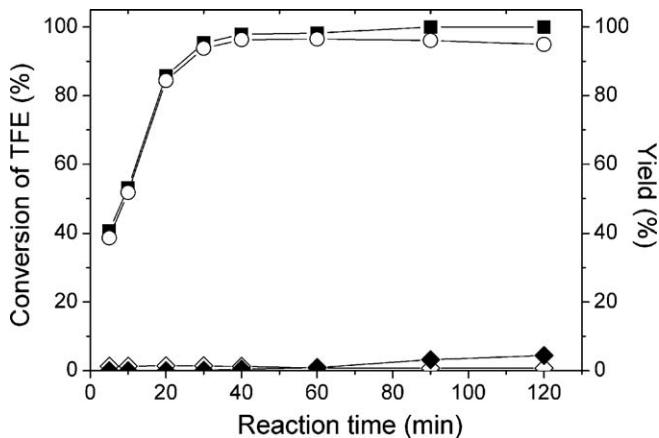
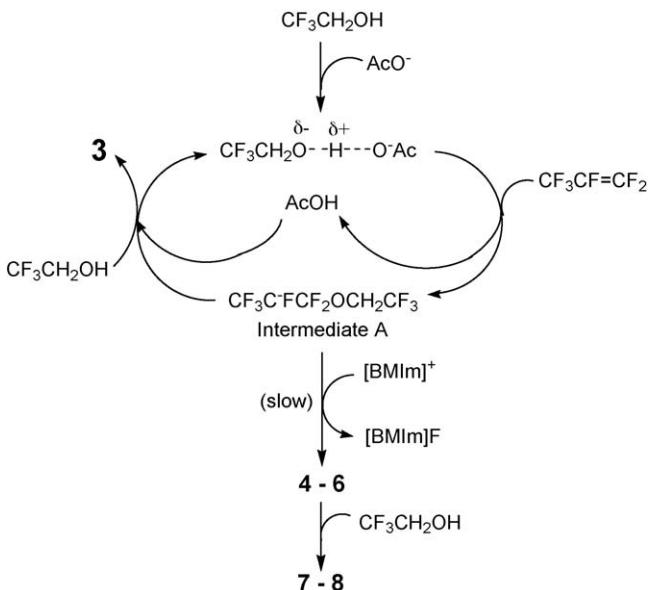
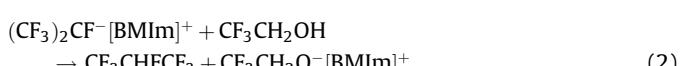


Fig. 1. Effect of reaction time for the hydroalkoxylation of HFP (molar ratio of TFE/[BMIm]AcO = 50, solvent = DMAc (10 mL), temperature = 25 °C): (▀) conversion of TFE, (○) yield of **3**, (◇) combined yield of **4–6**, and (◆) yield of **7–8**.



Scheme 3. A plausible mechanism for the formation of **3** and side products in the presence of [BMIm]AcO.

formation of small amounts of CF₃CHFCF₃ is considered as the result of the interaction of HFP with [BMIm]F formed in situ during the catalytic cycle followed by the reaction with TFE as in Eqs. (1) and (2) [20,23]:



4. Conclusions

Imidazolium-based ionic liquids with a basic anion such as CH₃CO₂[–], HCO₃[–], and CO₃^{2–} were highly effective for the hydroalkoxylation reaction of HFP with TFE to produce **3** in high yield while significantly reducing the formation of difficult-to-remove olefinic side product. The formation of side products could be further reduced either by increasing the electron density of

imidazolium ring or by increasing the rate of reaction using larger amounts of catalyst.

These novel imidazolium-based ionic liquid catalysts could be applied to the synthesis of other hydrofluoroethers in high yield and selectivity.

Acknowledgments

We acknowledge the financial support by a grant (AC3-101) from Carbon Dioxide Reduction & Sequestration Research Center, one of the 21st Century Frontier Programs funded by the Ministry of Science and Technology of Korean government.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.apcatab.2008.12.001](https://doi.org/10.1016/j.apcatab.2008.12.001).

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